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Structure and Thermal Expansion of Urea–Oxalic Acid (1:1)

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Abstract. Urea–oxalic acid, $CH_4N_2O.C_2H_2O_4$, monoclinic, space group $C2/c$, $a = 13{\cdot}0625\,(7)$, $b = 6{\cdot}6437\,(2)$, $c = 6{\cdot}8478\,(3)$ Å, $\beta = 92{\cdot}474\,(6)°$ [at 295 (1) K], $Z = 4$, $d_c = 1{\cdot}68$ Mg m^{-3}, $R_w = 5{\cdot}9\%$. The structure consists of layers of urea and oxalic acid molecules held together by hydrogen bonds. The thermal-expansion tensor has been calculated from the changes of the lattice constants with temperature. The elements of the thermal-expansion tensor at 295·1 K are $\alpha_1 = -1\,(5)$, $\alpha_2 = 29\,(6)$ and $\alpha_3 = 199\,(10) \times 10^{-6}$ K^{-1}.

Introduction. Urea can form two kinds of compounds with an acid: uronium salts (*e.g.* uronium nitrate) or addition compounds (*e.g.* urea–oxalic acid). It is possible to make two addition compounds from urea and oxalic acid: urea–oxalic acid (1:1) and urea–oxalic acid (2:1) (Dalman, 1934). The structure of the latter compound has been determined (Harkema, Bats, Weyenberg & Feil, 1973). We decided to determine the structure of urea–oxalic acid (1:1).

Crystals of urea–oxalic acid (1:1) were prepared by evaporation of a solution of 8 g urea and 84 g oxalic acid dihydrate in 220 ml water at 313 K (Dalman, 1934). The crystals have a pronounced cleavage plane which indicates a two-dimensional hydrogen-bonding network.

Data were collected on a Philips PW1100 automatic diffractometer at 295 (1) K. Reflexions with $3° < \theta < 35°$ were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) by the ω–2θ scanning technique. 1387 independent reflexions were measured, of which 1210 had $I > \sigma(I)$, $\sigma(I)$ being estimated from counting statistics. No correction for absorption was applied ($\mu = 0{\cdot}17$ mm^{-1}). The systematic extinctions hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$ ($h = 2n + 1$); $0k0$: ($k = 2n + 1$) correspond to space groups $C2/c$ or Cc (*International Tables for X-ray Crystallography*, 1952). We assumed $C2/c$, which was justified later.

Cell dimensions are listed in Table 1. There are four molecules of urea–oxalic acid (1:1) in the cell.

From the very strong $\bar{2}02$ reflexion it is clear that all molecules must be approximately parallel to $(\bar{1}01)$. As the general position in the space group $C2/c$ is eightfold, the oxalic acid molecules must lie on centres of inversion and the urea molecules on twofold axes. With the help of the known molecular geometries, different models of the structure were constructed, until an acceptable hydrogen-bonding scheme was found. Coordinates for the heavy atoms, obtained in this way, were used as input for the least-squares program.

The weighting scheme was the one normally used in our laboratory (de With, Harkema & van Hummel, 1976). Refinement with anisotropic temperature factors gave $R_w = 9{\cdot}0\%$ for all reflexions. A difference synthesis revealed the H atoms. Inclusion of the H atoms and refinement of their positions and isotropic temperature factors, together with the positions and anisotropic temperature factors of the other atoms, gave a final $R_w = 5{\cdot}9\%$. In the last stages of refinement a correction for isotropic secondary extinction was applied (Zachariasen, 1963; Larson, 1970).*

Final positional parameters are given in Table 2. The labelling of the atoms is given in Fig. 1, which shows a projection of the structure on the $(\bar{1}01)$ plane. Fig. 2 shows a stereoview of two parallel layers. Both figures were prepared with *ORTEP* (Johnson, 1965).

The bond distances and angles are given in Table 3.

To determine the thermal-expansion tensor, approximately 80 reflexions, distributed throughout reciprocal space and in the θ range 3–25°, were accurately centred. This procedure was repeated at six temperatures with the same crystal. The temperatures were stable within 1 K. Cell constants were optimized by a least-squares procedure from the Bragg angles. Results

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34223 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Lattice constants of urea–oxalic acid* (1:1) *at different temperatures*

T (K)	a (Å)	b (Å)	c (Å)	β (°)
295 (1)	13·063 (1)	6·6437 (3)	6·8478 (3)	92·47 (1)
259·5 (6)	13·033 (1)	6·6372 (4)	6·8158 (4)	92·10 (1)
221·6 (9)	13·002 (2)	6·6310 (8)	6·7820 (8)	91·71 (2)
183·4 (4)	12·977 (2)	6·626 (1)	6·749 (1)	91·36 (2)
146·5 (6)	12·952 (2)	6·6201 (6)	6·7218 (6)	91·01 (1)
107·6 (6)	12·931 (2)	6·6173 (9)	6·6944 (9)	90·65 (4)

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Table 2. *Final fractional atomic parameters*

E.s.d.'s in parentheses refer to the least significant digits.

	x	*y*	*z*
C(1)	0·0000 (0)	0·7859 (2)	0·2500 (0)
C(2)	0·2134 (1)	0·1655 (1)	0·4652 (2)
N(1)	0·0763 (1)	0·6856 (2)	0·3411 (2)
O(1)	0·0000 (0)	0·9758 (2)	0·2500 (0)
O(2)	0·1330 (1)	0·2345 (1)	0·3675 (1)
O(3)	0·2310 (1)	−0·0094 (1)	0·4997 (1)
H(1)	0·124 (1)	0·740 (3)	0·400 (3)
H(2)	0·079 (1)	0·559 (3)	0·341 (3)
H(3)	0·094 (2)	0·127 (3)	0·333 (3)

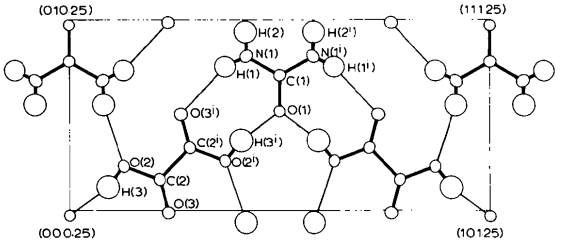

Fig. 1. Projection of the crystal structure of urea–oxalic acid (1:1) on ($\bar{1}$01). The vibration ellipsoids of the atoms are scaled to include 50% probability.

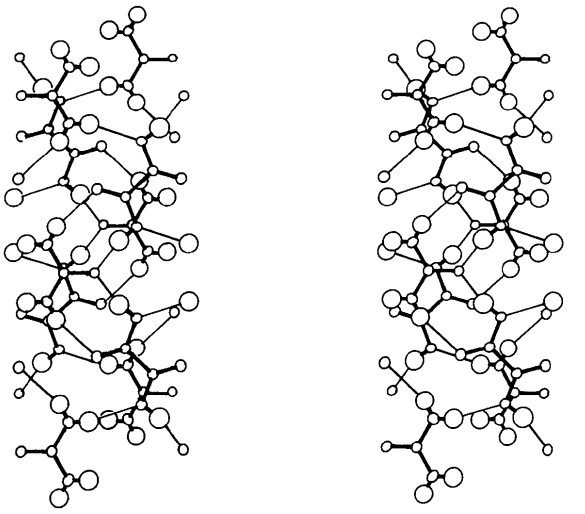

Fig. 2. Stereoview of two parallel planes of urea–oxalic acid (1:1). The viewing direction is perpendicular to ($\bar{1}$01). The vibration ellipsoids of the atoms are scaled to include 50% probability.

are collected in Table 1. The measured data have been fitted by a three-term polynomial in T by the method of least squares. Results are collected in Table 4. From the polynomials the elements of the expansion tensor and their e.s.d.'s at 295 (1) K are $\alpha_1 = -1$ (5), $\alpha_2 = 29$ (6) and $\alpha_3 = 199$ (10) $\times 10^{-6}$ K^{-1} (Nye, 1969). The direction cosines of the expansion tensor relative to the crystal axes are given in Table 5.

Discussion. The crystal structure consists of urea and oxalic acid molecules as in urea–oxalic acid (2:1). The acidic proton is attached to the oxalic acid molecule. The compound is therefore an addition compound and not a uronium salt. Urea and oxalic acid molecules are held together by a two-dimensional hydrogen-bonding network in the ($\bar{1}$01) plane. Hydrogen bonds are assumed whenever the O···H distance <2·4 Å (Olovsson, 1978). The dimensions of the hydrogen bonds are given in Table 3. The hydrogen-bonded layers of molecules are held together by van der Waals interactions. This difference in interactions explains why ($\bar{1}$01) is a perfect cleavage plane. The very strong anisotropy of the bonding forces between the molecules also explains the big differences in the lengths of the principal axes of the thermal-expansion tensor. Table 5 shows that the direction of the longest axis of the expansion tensor coincides with the normal to ($\bar{1}$01). Dimensions and orientation, with respect to the plane

Table 3. *Bond distances* (Å) *and angles* (°)

	Urea–oxalic acid (1:1) (*a*), (*d*), (*g*)	Urea–oxalic acid (2:1) (*h*), (*d*), (*g*)	Oxalic acid dihydrate (*b*), (*e*), (*g*)	Urea (*c*), (*e*), (*f*)
C(2)–C(2ⁱ)	1·537 (1)	1·537 (5)	1·536 (3)	
C(2)–O(2)	1·306 (1)	1·298 (5)	1·291 (5)	
C(2)–O(3)	1·206 (1)	1·208 (3)	1·212 (4)	
O(2)–H(3)	0·91 (2)	0·99 (4)	1·026 (7)	
C(1)–N(1)	1·332 (1)	1·329 (6)		1·352 (2)
C(1)–N(1ⁱ)	1·332 (1)	1·329 (4)		1·352 (2)
C(1)–O(1)	1·261 (2)	1·261 (3)		1·260 (3)
N(1)–H(1)	0·81 (2)	0·85 (2)		1·003 (4)
N(1ⁱ)–H(1)	0·81 (2)	0·83 (2)		1·003 (4)
N(1)–H(2)	0·84 (2)	0·87 (4)		0·998 (5)
N(1ⁱ)–H(2ⁱ)	0·84 (2)	0·88 (3)		0·998 (5)
O(1)–O(2ⁱ)	2·553 (1)			
N(1)–O(2ⁱ)	3·085 (1)			
N(1)–O(3ⁱ)	3·030 (1)			

	Urea–oxalic acid (1:1) (*a*), (*d*), (*g*)	Urea–oxalic acid (2:1) (*h*), (*d*), (*g*)	Oxalic acid dihydrate (*b*), (*e*), (*g*)	Urea (*c*), (*e*), (*f*)
C(2)–C(2ⁱ)–O(2ⁱ)	112·1 (1)	112·7 (3)	112·4 (3)	
C(2)–C(2ⁱ)–O(3ⁱ)	122·1 (1)	121·7 (2)	121·0 (3)	
O(2)–C(2)–O(3)	125·8 (1)	125·7 (2)	126·6 (3)	
C(2)–O(2)–H(3)	106 (1)	110 (3)	114·4 (6)	
O(1)–C(1)–N(1)	120·0 (1)	120·0 (3)		121·7 (1)
O(1)–C(1)–N(1ⁱ)	120·0 (1)	121·5 (2)		121·7 (1)
N(1)–C(1)–N(1ⁱ)	120·0 (1)	118·5 (3)		116·6 (1)
C(1)–N(1)–H(1)	124 (2)	118 (3)		119·0 (3)
C(1)–N(1ⁱ)–H(1ⁱ)	124 (2)	119 (2)		119·0 (3)
C(1)–N(1)–H(2)	122 (2)	123 (3)		120·2 (3)
C(1)–N(1ⁱ)–H(2ⁱ)	122 (2)	120 (2)		120·2 (3)
H(1)–N(1)–H(2)	115 (3)	119 (3)		120·8 (3)
H(1ⁱ)–N(1ⁱ)–H(2ⁱ)	115 (3)	119 (4)		120·8 (3)

Notes: (*a*) Present work. (*b*) Sabine, Cox & Craven (1969). (*c*) Pryor & Sanger (1970). (*d*) X-ray. (*e*) Neutron. (*f*) Corrected for thermal motion. (*g*) Not corrected for thermal motion. (*h*) Harkema, Bats, Weyenberg & Feil (1973).

Table 4. *Fit to the measured data of urea–oxalic acid* (1:1) $x = K_0 + K_1 T + K_2 T^2$

x	K_0	K_1 ($\times 10^3$)	K_2 ($\times 10^6$)	P*
a	12·885 (3)	0·32 (3)	0·96 (7)	0·9999
b	6·610 (3)	0·04 (3)	0·27 (6)	0·9988
c	6·625 (4)	0·57 (4)	0·63 (9)	0·9999
β	89·92 (4)	7·3 (4)	5·9 (9)	0·9999

* P is the correlation coefficient between measured and calculated unti-cell dimensions.

Table 5. *Direction cosines of the principal components of the expansion tensor (in columns) relative to the crystal axes of urea–oxalic acid* (1:1) *at room temperature*: 295 (1) K

The last column gives the direction cosines of the normal to ($\bar{1}01$).

α_1	α_2	α_3	
0·81	0·00	−0·59	−0·47
0·00	1·00	0·00	0·00
0·55	0·00	0·83	0·90

containing the hydrogen bonds, of the expansion tensor are comparable with the expansion tensor of oxamide, which also has a two-dimensional hydrogen-bonding network (de With, 1977).

Since the compound is an addition compound, one expects the bond lengths and angles to not differ significantly between the title compound, urea–oxalic acid (2:1), oxalic acid dihydrate and urea. Data on these compounds are given in Table 3, which shows that there is a fair agreement of bond lengths and angles in the different compounds. Some of the differences found, however, are significant from a crystallographic point of view. These differences, particularly in the urea molecules, may be due to differences in hydrogen bonding in the different compounds.

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Variabilities in interatomic distances and angles involving BeO_4 tetrahedra.

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Abstract

Variations in Be–O bond lengths have been found to be related to a large extent to corresponding variations of bond strength received by Be-bonded oxygens in 23 inorganic structures (r value for regression of Δd on $\Delta p_o = +0{\cdot}70$). An inverse relationship between Be–O lengths and Be–O–Si angles (in 17 beryllosilicates) is also largely valid when values of Be–O lengths uninfluenced by tetrahedral edge-sharing are considered ($r = -0{\cdot}59$). Be–O bonds unconnected with other tetrahedral atoms are rare, but the known ones are also relatively shorter than Be–O($\rightarrow T$) lengths. Because d–p π-bonding can be ignored for Be–O bonds and Be–O–T angles, their variations seem to indicate a more generalized applicability of the 'extended electrostatic valence rule'.

Variations in individual and average T–O distances and T–O–T angles (T = tetrahedral cation) have been known to exhibit, specially in the case of silicates and aluminosilicates, the following trends (Baur, 1961, 1971; Brown, Gibbs &

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